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Molecular constants of some planar XYZ_2 molecules and ions

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A fresh study of molecular force constants, generalized mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants has been attempted in nine molecules and ions belonging to the planar XYZ_2 type. The values of all these constants obtained here are found to be very reasonable. In particular, the close fit of the present values of centrifugal distortion constants with the corresponding observed values brings out the significance of the fresh procedure, involving kinetic constants, employed here in the study of the problem.

1. INTRODUCTION

The attention of molecular spectroscopists has been drawn to the concept of kinetic constants in molecules by Thirugnanasambandam (1964). These kinetic constants appear to be of basic significance in the study of molecular vibrations. They may be advantageously employed to obtain acceptable sets of force constants in polyatomic molecules in a simple manner The study of the planar XY_3 molecules, the bent symmetrical XY_2 molecules and the planar XY_4 molecules accomplished in this laboratory by Thirugnanasambandam *et al* (1969, 1974a, 1974b), has given rise to interesting results in relation to these three types of molecules.

Basically, the procedure adopted here is the well-known Wilson's FG matrix method (Wilson *et al* 1955) and the force field employed is the GQVFF. The freshness of the procedure involves two new aspects. The first one is provided by the physical meaning of the redundancy constraints (Ford & Orville Thomas 1967) relating to the force constants. The second one is related to the utilization of some of the kinetic constants in simplifying the secular equation and solving the same for the independent force constants in molecules.

This elegant method has been followed by Sanyal *et al* (1972) in their study of a few planar XY_4 cases while a large number of tetrahedral XY_4 molecules and ions has been investigated by Srivastava *et al* (1972) and Sanyal *et al* (1973, 1974a). Moreover, some CX_3^{2-} ionic systems have also been examined by Sanyal *et al* (1974b) and the utility of the kinetic constants in evaluating the force constants of polyatomic molecules is being increasingly recognised.

The present paper attempts to investigate yet another molecular type, viz., the planar XYZ_2 type, as an extention of the new procedure adopted here. Not only force constants but generalized mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants have all been studied here. These four classes of molecular constants evaluated in seven molecules and two ions, have led to interesting results in those cases. These results are very encouraging in as much as they not only confirm the well-established aspects of the problem but also give rise to fresh results of significance.

2. Theoretical Considerations

I. *F matrix* :

The choice of internal coordinates and the orientation of the principal axes are shown in figure 1

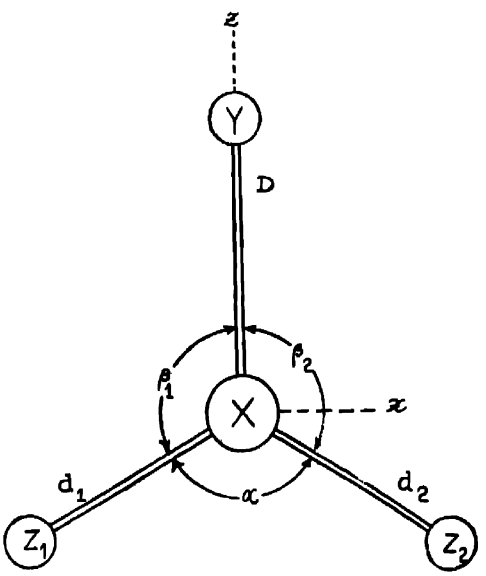

Fig. 1. Geometry of the planar XYZ_2 type molecule, the equilibrium bond distances and bond angles.

The symmetry coordinates used are essentially the same as those given by Oka & Morino (1963). Following Ford & Orville Thomas, the redundancy

constraints are utilized to reduce the general F matrix elements to the following simple forms :

A_1 *Species* :

$$F_{11} = f_D$$
$$F_{22} = f_a + f_{aa}$$
$$F_{33} = (3/\rho)(f_\beta + f_{\beta\beta})$$
$$F_{12} = 2^{\frac{1}{2}} f_{Da}$$
$$F_{13} = (3/2)^{\frac{1}{2}} f_{D\alpha}$$
$$F_{23} = -(3/\rho)^{\frac{1}{2}}(f_{a\beta}' + f_{a\beta}'')$$

B_1 *Species*

$$F_{44} = f_a - f_{aa}$$
$$F_{55} = (1/\rho)(f_\beta - f_{\beta\beta})$$
$$F_{45} = -(1/\rho)^{\frac{1}{2}}(f_{a\beta}' - f_{a\beta}'')$$

B_2 *Species*

$$F_{66} = f_\delta/\rho, \quad \rho \text{ being equal to } d/D.$$

The notations adopted for the force constants and the kinetic constants are identical and the number of primes on the interaction constants indicate the number of atoms common to both the internal coordinates.

II. *Kinetic constants*

Making use of Wilson's expression for the G matrix elements, the relevant G matrix elements and therefore the following expressions relating to the kinetic constants are obtained.

A_1 *Species*

$$K_{11} = k_D = m_y(m_x + 2m_z)/M$$
$$K_{22} = k_a + k_{aa} = m_z(m_x + m_y + 2s^2 m_z)/M$$
$$K_{33} = (3/\rho)(k_\beta + k_{\beta\beta}) = m_z(m_x + m_y + 2c^2 m_z)/3M$$
$$K_{12} = 2^{\frac{1}{2}} k_{Da} = -2^{\frac{1}{2}} c m_y m_z/M$$
$$K_{13} = (3/2)^{\frac{1}{2}} k_{D\alpha} = -6^{\frac{1}{2}} s m_y m_z/3M$$
$$K_{23} = -(3/\rho)^{\frac{1}{2}}(k_{a\beta}' + k_{a\beta}'') = -12^{\frac{1}{2}} c s m_z^2/3M.$$

B_1 *Species*

$$K_{44} = k_a - k_{aa} = m_z[D^2 m_x m_y + 2d^2 m_x m_z + 2(d - Dc)^2 m_y m_z]/I_y M$$
$$K_{55} = (1/\rho)(k_\beta - k_{\beta\beta}) = D^2 m_y m_z (m_x + 2s^2 m_z)/I_y M$$
$$K_{45} = -(1/\rho)^{\frac{1}{2}}(k_{a\beta}' - k_{a\beta}'') = 2Ds(d - Dc) m_y m_z^2/I_y M$$

$$K_{ss} = k_\delta/\rho \qquad = [(\rho - 1/c)^2/m_x + \rho^2/m_y + 1/2c^2 m_z]^{-1}$$

where $s = \sin\beta$, $c = \cos\beta$, m_i is the mass of the atom i, M is the mass of the molecule and I_y is the moment of inertia of the molecule with respect to the y-axis.

III. *Generalised mean square amplitudes*

The mean square amplitude matrix elements may be obtained using the relation (Cyvin 1968a)

$$\Sigma = L\Delta\tilde{L}$$

and therefrom the generalized mean square amplitudes may be calculated following the method of Morino & Hirota (1955).

IV. *Coriolis coupling constants*

The Coriolis matrix elements C_{ij}^{α} ($\alpha = x, y, z$) (Oka & Morino 1963) may be obtained by the vector method of Meal & Polo (1956) and the zeta matrix elements may be evaluated from the relation

$$\zeta^{\alpha} = L^{-1}C^{\alpha}(L')^{-1}$$

where L is the normal coordinate transformation matrix.

V. *Centrifugal distortion constants*

Cyvin *et al* (1968b) have reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of the partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of Kivelson & Wilson (1952, 1953). The quantities $t_{\alpha\beta\gamma\delta}$ are easily obtained using Cyvin's method.

3. Results and Discussion

Results relating to nine molecules and ions of planar XYZ_2 type are discussed here. Table 1 gives the molecular parameters and the spectral frequencies employed in the present investigation of molecular constants.

The kinetic constants and force constants are given in tables 2 and 3 respectively. It is interesting to note that the force constants $f_{D\alpha}$ and $f_{d\beta}'$ as well as the corresponding kinetic constants $k_{D\alpha}$ and $k_{d\beta}'$ are negative in all the molecules and ions. Moreover, the two isotopic pairs COH_2, COD_2 and CHO_2^-, CDO_2^- have nearly the same values for force constants. The carbon-halogen stretching force constants and indeed almost all the force constants in carbonyl and thiocarbonyl halides show uniform variations, decreasing with decreasing electronegativity of the halogen atoms. The C = O stretching force constant remains

Table 1. Structural parameters and vibrational frequencies (cm^{-1})

Sl. No.	Mol/Ion	D(Å)	d(Å)	β	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(B_1)$	$\nu_5(B_1)$	$\nu_6(B_2)$	Reference
1.	COH_2	1.204	1.102	121°40′	1746	2783	1500	2843	1249	1167	*a, b*
2.	COD_2	...	...	..	1700	2056	1106	2160	990	938	*a, b*
3.	CHO_2^-	1.06	1.25	116°30′	2828	1355	769	1590	1385	1062	*c, d*
4.	CDO_2^-	..	.		2130	1327	762	1580	1010	912	*c, d*
5.	COF_2	1.174	1.312	126°00′	1928	965	626	1249	584	774	*e, f*
6.	$COCl_2$	1.166	1.746	124°21′	1827	567	285	850	440	580	*e, g*
7.	$COBr_2$	1.13	2.05	125°00′	1828	425	181	757	350	512	*e, h*
8.	CSF_2	1.56	1.32	123°45′	1368	787	526	1189	417	622	*i*
9.	$CSCl_2$	1.56	1.75	124°21′	1137	505	220	816	294	473	*i*

a) Shimanouchi (1972)
b) Oka (1960a)
c) Landolt-Bornstein (1951)
d) Sugawara *et al* (1951)
e) Hopper *et al* (1968)
f) Laurie *et al* (1962)
g) Robinson (1953)
h) Overend *et al* (1959)
i) Hopper *et al* (1972)

sensibly the same in $COCl_2$ as well as $COBr_2$. However, this force constant f_D and the interaction force constant f_{Dd} have assumed enhanced values in COF_2; a similar behaviour is also noticed between CSF_2 and $CSCl_2$. Such enhancements appear to be a reflection of the relative differences relating to the concerned vibrational frequencies.

Additional data such as isotopic shifts, Coriolis coupling constants and centrifugal distortion constants have been employed to fix the force field in relation to COH_2 (Becher & Adrian 1971; Oka & Morino 1961), COF_2 (Kredentser & Sverdolov 1971) and $COCl_2$ (Becher & Adrian 1971; Mirri *et al* 1971). It is significant that the present force constnsts are in very good agreement with these values.

The generalized mean square amplitudes of vibration are reported in table 4 The molecule CSF_2 and the ions CHO_2^- and CDO_2^- have been studied here for the first time. Rajalakshmi & Cyvin (1966) and Ventkateswarlu *et al* (1967) have studied this problem in all other cases and the present results agree very closely with their values. The mean amplitudes of vibration also compare favourably wish published results (Muller & Nagarajan 1967; Muller *et al* 1968, Baran 1970). The values 0.0375, 0.0805 and 0.0922Å obtained for the mean amplitudes of C–O, C–H, O...H atom pairs compare well with the experimental electron diffraction values 0.0413, 0.0886 and 0.0915Å reported for COH_2 (Kato *et al* 1969).

Table 2. Kinetic constants (10^{-23} g)

S.No.	Mol/Ion	k_D	k_d	k_{Dd}	k_{dd}	k_α	k_β	$k_{D\alpha}$	$k_{d\alpha}$	$k'_{d\beta}$	k_δ
1.	COH_2	1.2403	0.1587	0.0468	0 0055	0.0354	0 0622	−0.0506	0.0017	−0.0112	0.0604
2.	COD_2	1.3293	0.3063	0.0877	0.0166	0.0676	0.1019	−0.0948	0.0063	−0.0329	0.0941
3.	CHO_2^-	0.1636	1.6065	0.0265	0.6736	0.2542	0.1080	−0.0355	0.2513	−0.1741	0.0780
4.	CDO_2^-	0.3198	1.6478	0.0519	0.6403	0.2615	0.1389	−0.0694	0.2458	−0.2039	0.1074
5.	COF_2	2.0121	2.2348	0.4494	0.2923	0.4368	0 3752	−0.4124	0 2879	−0.4926	0.2273
6.	$COCl_2$	2.2221	3.5588	0.5351	0.9273	0.6622	0.5233	−0.5220	0.6439	−0.8429	0.2311
7.	$COBr_2$	2.4272	6.4808	0.6469	2.9620	1 2525	0.8572	−0.6160	1.7432	−1.7361	0.2354
8.	CSF_2	3.2380	2.4017	0.6836	0.3014	0.4763	0 4518	−0 6820	0.2252	−0.5452	0.2033
9.	$CSCl_2$	3.8187	4 0102	0.9196	0 6610	0.7503	0 6701	−0.8970	0.5535	−1.0013	0.2381

Table 3. Force constants (10^5 dynes cm^{-1})

S.No.	Mol/Ion	f_D	f_d	f_{Dd}	f_{dd}	f_α	f_β	$f_{D\alpha}$	$f_{d\alpha}$	$f_{d\beta}'$	f_δ
1.	COH_2	13.2108	4.3697	0 4987	0.0692	0.2825	0.3640	−0.4040	0.0134	−0.0638	0.2920
2.	COD_2	12.8581	4 6221	0 3113	0 0968	0 2932	0.3676	−0 4114	0 0272	−0 1170	0.2936
3.	CHO_2^-	4.3922	10.4297	0.1475	2.2471	0.5333	0.3822	−0.0745	0 5273	−0.5425	0 3120
4.	CDO_2^-	4.6485	10.2594	0.2820	2.1752	0.5388	0.3826	−0.1429	0.5065	−0.5299	0.3171
5.	COF_2	16.2440	7.2463	1.3696	0.4550	0 6074	0 4760	−0.5734	0.4003	−0.6236	0 4831
6.	$COCl_2$	13.6244	4.0511	0.4894	0.0522	0.1908	0.2606	−0.1504	0.1856	−0.4219	0.2758
7.	$COBr_2$	13.3224	3.6157	0.2446	−0.0457	0.1456	0.1917	−0 0716	0.2026	−0.3808	0.2189
8.	CSF_2	11.5911	5.6989	1.4541	0.0515	0.4676	0.3155	−0.6696	0.2210	−0.3741	0.2790
9.	$CSCl_2$	6.9543	3.6044	0.7444	0.1767	0.1288	0.1771	−0.1540	0.0951	−0.2675	0.1890

Table 4. Generalized mean square amplitudes (10^{-3}Å^2) at 298.16°K

Sl.No.	Mol/Ion	Distance	$<\Delta z^2>$	$<\Delta x^2>$	$<\Delta y^2>$	$<\Delta z\,\Delta x>$
1.	COH_2	C—O	1.3950	0.5742	0.4939	0
		C—H	6.4439	12.1002	8.0529	−0.0034
		O...H	8.6278	7.8803	4.5583	−2.4898
		H...H	15.1413	19.9524	0	0
2.	COD_2	C—O	1.3936	1.0584	0.9692	0
		C—D	4.6631	8.0740	5.6866	0.0197
		O...D	6.2663	4.5857	1.9606	−1.4329
		D...D	10.5583	11.9143	0	0
3.	CHO_2^-	C—H	6.4149	12.7280	13.5421	0
		C—O	1.6262	2.0917	0.8064	−0.0422
		H...O	9.2552	10.5731	7 7390	2.3088
		O...O	2.1688	0.1517	0	0
4.	CDO_2^-	C—D	4.6006	9.0644	7.8760	0
		C—O	1.6378	2 1123	1.3105	−0.0368
		D...O	6.7537	7.1659	2.7611	1.5617
		O...O	2.1836	0.2598	0	0
5.	COF_2	C—O	1.2804	3.1554	2.5985	0
		C—F	1 9003	2 4373	2.1882	0.0620
		O. .F	2.4585	1 6271	0.0176	−1.3512
		F.. F	2.5975	1 4906	0	0
6.	$COCl_2$	C—O	1.3517	4.9141	4.0889	0
		C—Cl	2.4277	4.0664	2.7059	0.0678
		O...Cl	3.3598	3.7311	0.1422	0.0611
		Cl ..Cl	4.2436	0.7478	0	0
7.	$COBr_2$	C—O	1.3532	6.5731	5.1128	0
		C—Br	2.4808	5.0084	2 8777	−0.0898
		O...Br	3.9577	5.5974	0.3190	0.2663
		Br...Br	4.6696	0.2532	0	0
8.	CSF_2	C—S	1.4233	2.9167	2.6425	0
		C—F	2.1352	3.4305	3.1087	0.0027
		S...F	2.7272	1.3141	0.0189	0.0031
		F ..F	3.0783	3.3230	0	0
9.	$CSCl_2$	C—S	1.7442	5.1488	4.2697	0
		C—Cl	2.5667	5.9439	3.9739	0.0891
		S...Cl	3.8620	3.8982	0 0053	−0.4320
		Cl...Cl	5.9655	2.3899	0	0

The calculated values of the Coriolis coupling constants and the centrifugal distortion constants are given in tables 5 and 6 respectively. The zeta values obey the relevant sum rules. The centrifugal distortion constants of $COBr_2$, CHO_2^- and CDO_2^- are presented here for the first time. It may also be seen from table 6 that the calculated τ-values compare closely with those determined experimentally, lending further support to the fact that the present values are reasonable.

Table 5. Coriolis coupling constants.

S.No.	Mol/Ion	ζ_{16}^{x}	ζ_{26}^{x}	ζ_{36}^{x}	ζ_{14}^{y} ζ_{15}^{y}	ζ_{24}^{y} ζ_{25}^{y}	ζ_{34}^{y} ζ_{35}^{y}	ζ_{46}^{z}	ζ_{56}^{z}
1.	COH_2	−0.3998	0.5433	−0.7382	−0.2408 0.3697	0.0700 −0.9156	−0.9680 −0.1582	−0.8489	0.5285
2.	COD_2	−0.3311	0.6679	−0.6666	−0.2705 0.1924	0.2044 −0.9460	−0.9408 −0 2609	−0.8532	0.5216
3.	CHO_2^-	−0.8922	0.2963	−0.3410	−0.2398 0.9617	0.4492 −0.0112	−0.8606 −0.2738	−0.6405	0.7680
4.	CDO_2^-	−0.8678	0.3019	−0.3946	−0.3394 0.9294	0.4061 0.0053	−0.8485 −0.3692	−0.7520	0.6592
5.	COF_2	−0.9028	0.2949	−0.3130	−0.6381 0.7194	0.2655 −0.1289	−0.7227 −0.6825	−0 8806	0.4738
6.	$COCl_2$	−0.9352	0.2644	−0.2354	−0.6904 0.7020	0.3627 0.1265	−0.6259 −0.7009	−0.8890	0.4580
7.	$COBr_2$	−0.9579	0.2426	−0.1532	−0.7337 0.6720	0.4744 0.4008	−0.4864 −0.6226	−0.8924	0.4511
8.	CSF_2	−0.9002	0.2531	−0.3543	−0.7199 0.6162	0.1424 −0.3192	−0.6793 −0.7199	−0.9248	0.3805
9.	$CSCl_2$	−0.9473	0.1879	−0.2594	−0.7862 0 5942	0.1900 −0.0295	−0.5881 −0 8038	−0.9330	0.3599

Table 6. Centrifugal distortion constant (MHz)

Sl.No.	Mol/Ion	τ_{aaaa}	τ_{bbbb}	τ_{aabb}	τ_{abab}
1.	COH_2	−92.4027	−0.3643	0.9275	−3.3726
		−101.831	−0.3922	1.4101	−3.2920*a*
		—	−0.3837	1.7988	— *b*
			±0.0150	±0.1499	
2.	COD_2	−21 8515	−0.2878	0.6672	−1.7418
		−25.4940	−0.3194	0.9273	−1.7808*a*
3.	CHO_2^-	−19.2043	−0.0385	0.4297	−0.1184
4.	CDO_2^-	−6.7060	−0.0389	0.2418	−0.1302
5.	COF_2	−0.05542	−0.04172	0.01849	−0.03522
		−0.06539	−0.04517	0 02467	−0.03558
		±0.00009	±0 00009	±0.00086	±0.00044*c*
6.	$COCl_2$	−0.05072	−0.00660	0.01055	−0.00518
		−0.04097	−0.00675	0.00830	−0.00573*d*
		±0.00028	±0 00004	±0.00020	±0.00009
7.	$COBr_2$	−0.0355	−0.0006	0.0030	−0.0008
8.	CSF_2	−0.0604	−0.0066	0.0071	−0.0198
9.	$CSCl_2$	−0 0079	−0.0097	0.0058	−0.0015

a—Oka *et al* (1960b)
b—Toth (1973)
c—Mirri *et al* (1969)
d—Mirri *et al* (1971)

3. Conclusion

A fresh attempt has been made to evaluate all the general quadratic force constants of nine planar XYZ_2 type molecules and ions. The values of the force constants and other molecular constants appear to be highly reasonable. It is thus seen that the kinetic constants do play a fundamental role in molecular dynamics and a recognition of the same leads to acceptable sets of molecular constants.

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